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Thermal effects on the magnetic properties of titanium modified cobalt ferrite

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The temperature dependence of the magnetic properties of titanium modified cobalt ferrite is presented. The change of maximum magnetization obtained at $H \approx 2.4$ MA/m between any two temperatures increases systematically with composition, which is desirable for applications in devices. Variation in magnetocrystalline anisotropy and coercivity were different from previous studies on cation substituted cobalt ferrite. At lower concentrations, the effect of lower thermal energy dominated the effect of non-magnetic cation substitutions in controlling the anisotropy. The reverse was the case at higher concentrations. The temperature dependence of coercivity is dominated by the contribution of magnetocrystalline anisotropy to coercivity, while the compositional dependence of coercivity is dominated by microstructural contribution through the pinning of domain walls. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919229>]

I. INTRODUCTION

In most cases, materials do not naturally occur in a state suitable for direct applications. Consequently, the ability to tailor their properties towards the applications of interest is necessary. Spinel structured oxide materials have a suitable crystal structure, which allows for such tailoring by chemical modifications usually by elemental substitutions. One can take advantage of the antiparallel coupling of the magnetic moments of cations on the tetrahedral sites (A-sites) and octahedral sites (B-sites) to systematically adjust the magnetic properties of spinel structured ferrites, such as cobalt ferrite. Properties such as saturation magnetization, coercive field, remanent magnetization, magnetocrystalline anisotropy, magnetostriction amplitude, Curie temperature, and strain sensitivity can all be controlled by such chemical modifications. In addition, the chemical and thermal stability of the materials and the fact that they are better suited for high frequency applications than intermetallic based materials further enhance their technological potential.

It was found in the previous studies that magnetization, Curie temperature and even electrical properties of cobalt ferrite can be controlled in a remarkably linear pattern by Ti^{4+} substitution for Fe^{3+} .^{1,2} An inverse relationship, also dependent on the rate of co-substitution of $\text{Ti}^{4+}/\text{Co}^{2+}$, was reported for susceptibility and coercive field.^{2,3} Nevertheless, the temperature dependence of the magnetic properties of titanium modified cobalt ferrite is not currently well understood. This is important for understanding the temperature dependence of other magnetic field controlled properties, such as magnetoelasticity. In $\text{Ge}^{4+}/\text{Co}^{2+}$, it was shown that the changes in magnetoelastic properties with temperature could be explained by changes in magnetic properties with temperature.⁴ Hence, this study focuses on the temperature dependence of magnetic properties in $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substituted cobalt ferrite.

II. EXPERIMENTAL DETAILS

Samples were prepared via the traditional ceramic method. The sample preparation, compositions, and structural properties have been previously reported.² In brief, they were confirmed to be single spinel phase materials using scanning electron microscopy (SEM) and x-ray diffractometry. The samples have lattice parameters between 8.37 and 8.40 Å with compositions being very close to targeted $x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.5 in $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$.² In this work, the magnetic properties were studied from 50 to 300 K using a vibrating sample magnetometer (VSM). Magnetocrystalline anisotropy was determined by the law of approach to saturation magnetization as discussed in the literature.^{5,6}

III. RESULTS AND DISCUSSION

Fig. 1 shows that magnetization is strongly dependent on composition at all temperatures.

In Fig. 2(a), it is shown that the maximum value of magnetization, $M_{@3T}$, varied linearly with composition at all temperatures. The dependence of the magnetization of $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ on composition has been previously explained, for data obtained at 300 K,² to be due to both the site preference of the cations and their magnetic moments. Ti^{4+} and Co^{2+} have stronger preferences for the B-sites than Fe^{3+} but the sum of their magnetic moments is lower than that of Fe^{3+} . Since the net magnetic moment in spinel structured materials is $m = \sum m_{B\text{-sites}} - \sum m_{A\text{-sites}}$, co-substitution of $\text{Ti}^{4+}/\text{Co}^{2+}$ results in lower magnetization. $\sum m_{B\text{-sites}}$ is the magnetic moment of the B-site cations and $\sum m_{A\text{-sites}}$ is magnetic properties of the A-site cations.

Also, in Figs. 2(a) and 2(b), at $x = 0$, there is little variation in magnetization at all temperatures. Although magnetic field of $H \approx 2.4$ MA/m was insufficient to saturate the magnetization at temperatures lower than 300 K, a similar observation was made in the previous study in which up to $H \approx 4$ MA/m was applied.⁷ An interesting observation in Fig. 2(b) is that the rate

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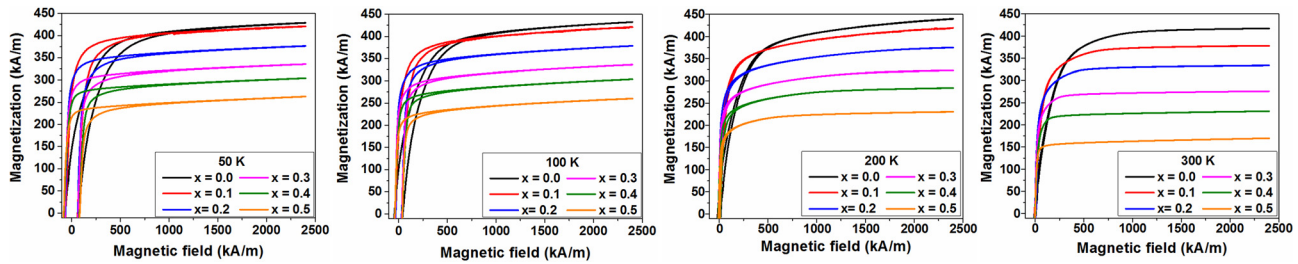


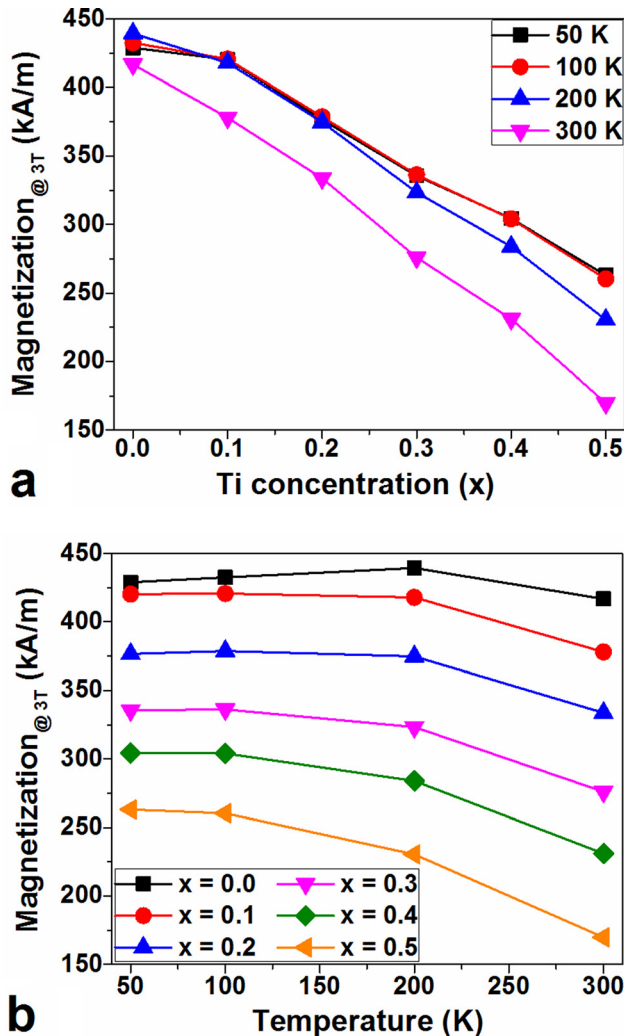
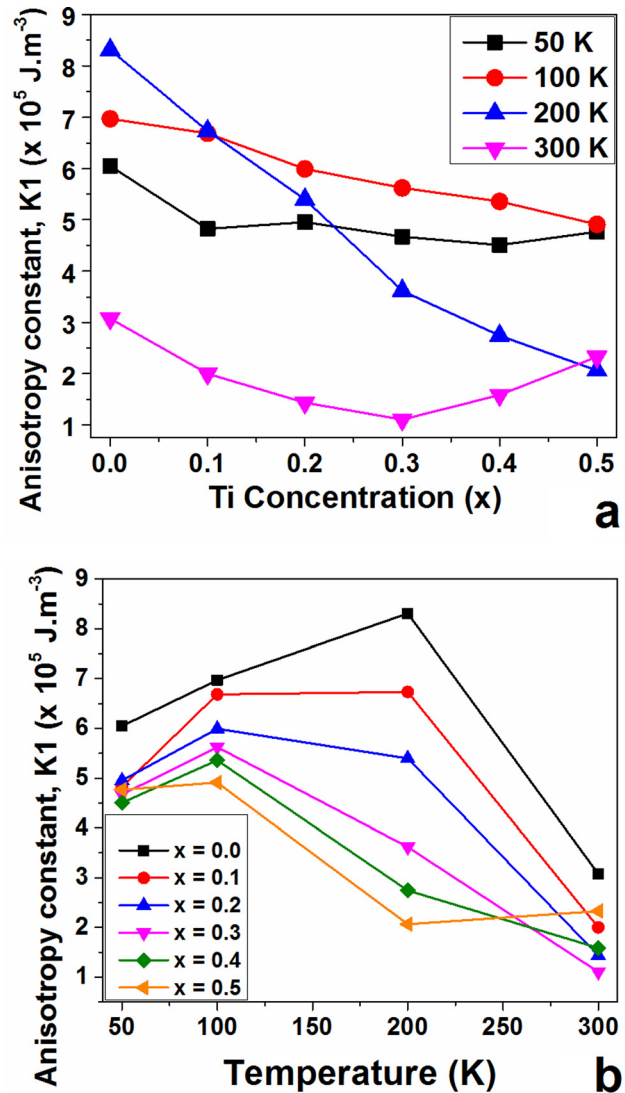
FIG. 1. Magnetization as a function of magnetic field for the samples measured from 50 to 300 K.

at which the maximum value of magnetization ($M_{@3T}$) reduces between any two temperatures, increases with composition. This systematic variation is desirable for device applications.

At each temperature in Fig. 3(a), it can be seen that magnetocrystalline anisotropy decreased with $\text{Ti}^{4+}/\text{Co}^{2+}$ concentration, comparing the substituted and the un-substituted samples. With increase in the concentration of $\text{Ti}^{4+}/\text{Co}^{2+}$, the variation in magnetocrystalline anisotropy becomes increasingly temperature dependent as can be readily seen in Fig. 3(b). At 50 K, increasing concentration from $x = 0.1$ to 0.5 had no significant effect on the magnetocrystalline anisotropy. However, at 100 K, magnetocrystalline anisotropy decreased

slightly and even more significantly at 200 K. At 300 K, it decreased for compositions up to $x = 0.3$ and then increased. This systematic variation is not reported in previous cation substituted cobalt ferrite studies.

It is known that non-magnetic cations weaken the exchange interaction between the cations on the A- and B-sites resulting in lower magnetocrystalline anisotropy. It is also known that high temperatures reduce anisotropy. On the other hand, the high magnetocrystalline anisotropy in Co-based ferrites is mainly due to the unquenched orbital angular

FIG. 2. Maximum magnetization as a function of (a) $\text{Ti}^{4+}/\text{Co}^{2+}$ concentration and (b) temperature.FIG. 3. (a) Compositional and (b) temperature dependence of magnetocrystalline anisotropy constant, K_1 , in $\text{Co}_{1-x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0-0.5$).

momentum of the Co ions. In most of the previous works on cation substituted cobalt ferrite, non-magnetic cations were substituted without additional Co ions. Hence, in those works, magnetocrystalline anisotropy generally decreased with increasing concentration of non-magnetic cations and temperature. In the present work, however, non-magnetic Ti is co-substituted with magnetic Co ions. Hence, while Co ions tend to increase magnetocrystalline anisotropy, Ti ions tend to decrease it. This resulted in comparable magnetocrystalline anisotropy at all compositions (up to $x = 0.5$) for measurements at 50 K. At 100 K and 200 K, both higher thermal energy and higher concentration of non-magnetic Ti ions outweighs the effect of Co ions in enhancing anisotropy, hence the observed reduction of magnetocrystalline anisotropy which continued up to $x = 0.3$ at 300 K, beyond which anisotropy increased. This increase may be related to change in the site distribution of cations at higher temperatures.

Based on the explanation provided for the variation shown in Fig. 3(a), one would expect that in Fig. 3(b), anisotropy should decrease for all compositions as temperature increases. A similar trend as in Fig. 3(b) is often observed in non-magnetic cation substituted cobalt ferrite studies. The decrease in anisotropy below 200 K at $x = 0.0$ has been explained to be related to the anisotropy field becoming comparable or higher than the maximum applied magnetic field at lower temperatures. This can be seen in Fig. 1 because below 300 K, ~ 2.4 MA/m could no longer saturate the magnetization of the samples, irrespective of composition. In Fig. 3(b), as $\text{Ti}^{4+}/\text{Co}^{2+}$ substitution level increases, lower anisotropy due to high concentration of non-magnetic Ti^{4+} cations causes this effect to gradually occur at lower temperatures. For example, at $x = 0.5$, it occurred at 50 K. In this study, temperature changes dominate the variation in the magnetocrystalline anisotropy at lower cation concentration. However, at higher concentrations, the contribution due to cation substitution dominates.

It can be seen in Figs. 4(a) and 4(b) that coercivity decreased with temperature for each composition. This is similar to the previous reports on cation substituted cobalt ferrite.^{5,7-9} Two factors that can contribute to coercivity are magnetocrystalline anisotropy and microstructural pinning sites which obstruct domain activities. Considering the dependence of coercivity on temperature, Fig. 4(b) suggests that coercivity is dominated by magnetocrystalline anisotropy. This is because as thermal energy increases, magnetocrystalline anisotropy decreases hence its contribution to the measured coercive field decreases. One would expect the trend in the dependence of magnetocrystalline anisotropy on composition in Fig. 3(a) to be similar to that of coercivity in Fig. 4(a). This would be true only when the contribution by magnetocrystalline anisotropy to coercivity dominates. However, a nearly opposite trend, which is atypical of the previous studies on cation substituted cobalt ferrite,^{5,7} is observed. This indicates that rather than magnetocrystalline anisotropy, the changes in coercivity with composition are dominated by another factor, which is, in turn, temperature dependent and is likely microstructurally related.

Although the samples used in the present study are single phase, the SEM micrographs show significantly higher porosities

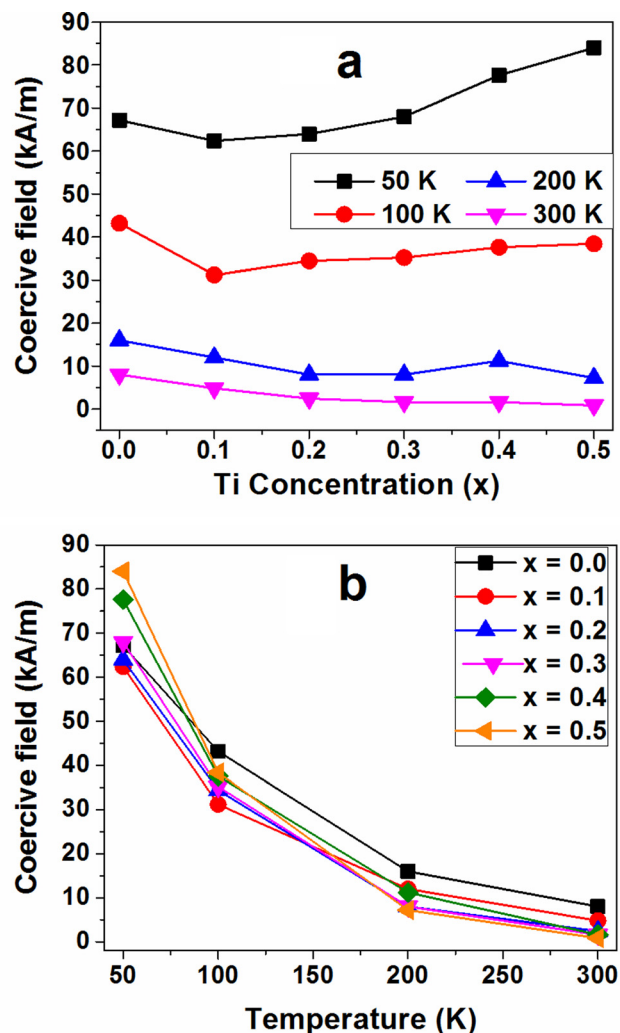


FIG. 4. Variation of coercive field with (a) composition and (b) temperatures in $\text{Co}_{1-x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0-0.5$).

with cation substitution.² In Fig. 4(a), it seems that the microstructural contribution to coercivity through the pinning of domains is high enough that the contribution by magnetocrystalline anisotropy is negligible. Hence, at 300 K and 200 K, coercivity is nearly insensitive to compositional changes, while magnetocrystalline anisotropy is sensitive to compositional changes (Fig. 3(a)). At 100 K, coercivity increases with composition and even increases at a higher rate at 50 K. This may be due to further microstructural defects such as cracks generated as a result of thermal shocks when samples are swept from higher to lower temperatures. Thermal shock is a well-known drawback in the technological applications of ferrites.¹⁰ This degradation of microstructure by thermal shock is dependent on multiple factors such as the grain sizes, the size and distribution of pores and cracks, and types and distribution of grain boundaries.¹¹ It appears that in this study, a temperature sweep rate of 20 deg/min resulted in thermal shocks causing the microstructural contribution to coercivity to dominate the magnetocrystalline anisotropy contribution at 100 K and 50 K, hence the observed increase in coercivity. Therefore, the temperature dependence of coercivity is dominated by magnetocrystalline anisotropy while the compositional dependence of coercivity is dominated by microstructure.

IV. CONCLUSIONS

An investigation of the dependence of the magnetic properties of $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substituted cobalt ferrite shows a strong and systematic dependence of magnetization on composition and temperature. The variation of magnetocrystalline anisotropy and coercivity in this study are atypical compared with previous studies. Results were explained considering thermal, anisotropy, and magnetic energies, in addition to microstructural effects and cation distribution.

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